Sulfonated Polystyrene grafted Nafion® Electrolyte Membranes for Direct Methanol Fuel Cells

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Fuel cells are long-term stable power sources not necessarily requiring electron charging and discharging cycles. Polymer electrolyte membrane is one of most important components in polymer electrolyte fuel cells (PEFC). Perfluorocarbon type membranes such as Nafion® (Du Pont), XUS (Dow) and Aciplex-S® (Asahi), etc. are well known commercial electrolyte membranes [1].

Although these commercial polymer electrolyte membranes are reported to possess good physico- and electrochemical properties such as high proton conductivity, high thermal, mechanical, and chemical resistance, there are some problems to solve in order to be applied in direct methanol fuel cell (DMFC). Among them, the critical one is the methanol crossover from anode to cathode, which ultimately results in the reduction of proton conduction efficiencies.

There have been a lot of researches to prohibit or reduce the methanol crossover. Ones of researches conducted based on using Nafion® membranes include i) preparation of composite electrolyte using a film of metal hybrid (N/Pt/Pd/Pt/N) [2], ii) doping with metal ion like Ce^{+} in Nafion® membranes [3], and iii) surface treatment of Nafion® membranes [4]. Those methods, however, could not satisfy the preparation cost and cell performances.

In this study, the plasma surface modification technique was applied to Nafion® membranes to reduce the methanol crossover in DMFC application. Nafion® membrane surfaces were modified by styrene plasma to induce grafting polymerization. Surface grafting polymerization was initiated via argon or benzene plasma treatment. This plasma produced radicals on Nafion® membrane surfaces and styrene monomers were successively introduced to have high molecular weight. After the polystyrene (PS) was grafted on the membranes surfaces, those were sulfonated to improve ion conductivity. The solution of chlorosulfonic acid in 1,2-dichloroethane, 10 vol %, was used as sulfonation agent. Fig. 1 shows the plasma treatment apparatus.

Chemical structure and morphology of the sulfonated PS-grafts on Nafion® membrane surfaces were characterized using FTIR, SEM and XPS. Ion conductivity was measured using impedence spectroscopy, and methanol permeability was measured using a permeation test cell specially designed. Thermal and mechanical properties were also investigated.

The permeation test apparatus was composed of two compartments - one water and the other aqueous methanol solution in 2 mol % - separated by a membrane. Fig. 2 shows the methanol concentration in water compartment according to diffusion time. The rate of methanol concentration change significantly reduced when the sulfonated PS-grafted Nafion® membrane was replaced for commercial Nafion® membrane. The proton conductivity of sulfonated PS-grafted Nafion® membranes was slightly lower than that of commercial Nafion® membranes

References

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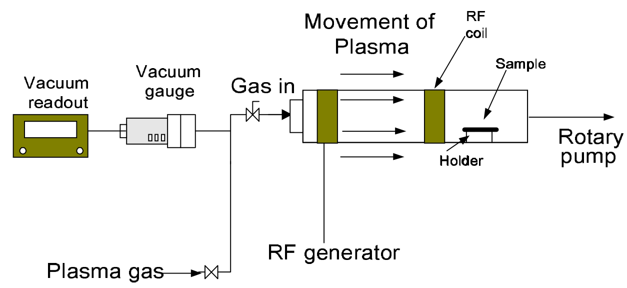

Fig. 1. Reactor for plasma surface treatment for grafting polymerization.

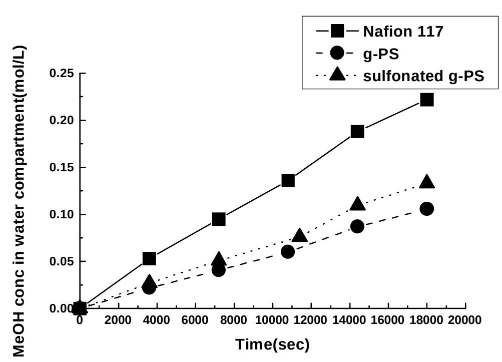

Fig. 2. Methanol concentration in water compartment as a function of diffusion time for Nafion® 117, PS-grafted Nafion®, and sulfonated PS-grafted Nafion® membranes, respectively.